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FE-2018-4

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Quarterly Progress Report, March 11—June 10, 1976

T. Houser

July 1976

Work Performed Under Contract E(49-18)-2018

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MASTER

ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

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Printed in the United States of America
USERDA Technical Information Center, Oak Ridge, Tennessee

FE-2018-4
Distribution Category UC-90e

FUNDAMENTALS OF NITRIC OXIDE FORMATION IN FOSSIL FUEL COMBUSTION

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Date Published - July 1976

Prepared for the United States
Energy Research and Development Administration

Under Contract No. E(49-18)-2018

ABSTRACT

A study of the reaction mechanism which leads to NO formation from fuel nitrogen by determining the rate and mechanism of pyridine pyrolysis was continued. In addition to the previously reported volatile products, hydrogen was found in the reactor exit stream. It was found that as the reactor's surface to volume increased, the pyrolysis rate decreased indicating radical recombinations play an important role in the rate of the reaction. The addition of cyanogen to the carrier gas increased the rate significantly. Both the surface and cyanogen effects indicate a chain mechanism may be operating. The mechanistic implications of the data from this program and from related investigations are reviewed.

OBJECTIVE AND SCOPE

One of the major scientific problems confronting society today is the reduction and control of air pollution. The emission of NO and other oxides of nitrogen from various combustion devices is a serious contributor to that pollution. The source of NO during the combustion process may be atmospheric nitrogen or nitrogen-containing compounds in the fuel. In order to predict NO emission for the formulation of suitable analytical models, it is necessary to have accurate kinetic data and a reasonable reaction mechanism for the formation of NO.

The objective of this research program is to obtain kinetic and product distribution data from which a mechanism may be proposed for the formation of NO from fuel nitrogen. Specifically, the kinetics of the pyrolysis and oxidative pyrolysis of pyridine (since it is representative of the nitrogen-containing components of fossil fuels) will be studied. In addition, similar oxidative studies will be made on representative, condensed-ring heterocycles, e.g. quinoline, carbazole, etc. to determine the extrapolatability of the results obtained with pyridine to more coal like structures. The oxidation of volatile, nitrogen-containing pyridine pyrolysis products, e.g. cyanogen, HCN, vinylcyanide, etc., will also be carried out to help elucidate the mechanism of NO formation.

The experimental approach will involve the use of a stirred-flow reactor to obtain differential rate data which will aid in interpretation of complex kinetic data. On stream mass spectrometric, gas chromatographic and infrared spectrophotometric monitoring of products and reactants will be carried out also.

SUMMARY OF PROGRESS

Task 2, which consists of experiments to determine the rate and mechanism of pyrolysis of pyridine in an inert atmosphere, has been about 90% completed. Although additional data have been obtained during the quarter, it is evident that a more careful analysis of products is warranted before an understanding of a pyrolysis mechanism can be obtained. This quarter's work has concentrated on a better definition of products, with nothing significantly new to report. However, an analysis of the significance of the results to date, their consistency with previous results and their influence on previously proposed mechanisms is discussed. In addition, experiments to determine surface effects and the influence of added cyanogen on the rate were carried out. As the surface to volume ratio of the reactors increased, the reaction rate decreased significantly, indicating that radical recombinations were influential on the rate of pyridine consumption. The addition of cyanogen to the carrier gas was found to increase the pyrolysis rate significantly. These observations indicate that the reaction mechanism is radical chain and/or sequential.

Task 4, which is concerned with the oxidation of nitrogen-containing intermediate species has continued with the study of the oxidation of cyanogen. Rates at two additional initial reactant concentrations were measured, the results are consistent with those reported previously.

DETAILS OF TECHNICAL PROGRESS

Task 2

Work concentrated on the continued identification of the volatile products from the pyrolysis of pyridine. In addition, the effects of added cyanogen and variation in reactor surface area were investigated. Finally, consideration is given to the pyridine pyrolysis mechanism based on the information available from this and other studies (1-4).

Volatile Products. Attempts to better separate and identify the volatile products from the pyrolysis were not fruitful. A new column (5% dinonylphthalate in chromosorb-W AW) to be used in the department's MS-GC (Dupont Model 21-490B) which should give better product separation has been ordered; the column currently on the MS-GC did not give a satisfactory separation and clear identification could not be made. The mass spectra obtained were consistent with those data previously reported (1c), with the addition of significant amounts of hydrogen found in the non-condensible fraction.

Experimental conditions were altered for the flow system and the chromatograph attached to the flow system to determine the optimum conditions for product analysis and to investigate shifts in relative product yield. It was found that at least five product peaks were formed at 900°C when the extent of reaction was as high as 77%, contrary to the previous report that no volatile products were found below 950°C(1c). When the reaction temperature was 1000°C (93% reaction) the same five peaks appeared plus a little shoulder between the first two, which may be buten-3 yne (C_4H_4). Some mass spectral evidence

for this compound had been found previously but the chromatographic peak had not been observed. These five product peaks are the same as those reported earlier (1c). The second, fourth and fifth peaks are primarily HCN, vinyl cyanide and benzene resepectively, the first may be a mixture of methane, acetylene and ethylene, the third is still unknown. A comparison of the relative amounts of these products from peak heights indicates that an increase in temperature increased the first somewhat (about 50% higher), the second and third were larger by a factor of 2.5, and the fourth and fifth changed very little. The large increase in HCN is consistent with the work of Axworthy and co-workers (2).

Another point of interest is that a liquid nitrogen trap in the flow line before sampling completely eliminated peaks 2 to 6 (the last being reactant) from the chromatograms and reduced the first by more than a factor of four. This is taken as evidence that the first peak is less than 50% methane and/or ethylene; the remainder of peak one may be acetylene.

Work is continuing on the more complete identification of products and their shifts with temperature.

Surface and Additive Effects. Three reactors were used with significantly different diameters, which gave rise to the following surface to volume ratios: large volume 64.3 cc, SA/V = 1.99 cm^{-1}, medium volume 39.2 cc, SA/V = 2.73 cm^{-1}, small volume 6.5 cc, SA/V = 8.97 cm^{-1}. The rate data from these three reactors at 975° and 1000°C are summarized in Table 1 (data for the medium reactor were reported previously, 1b). It can be seen that there is a decrease in rate as the surface area/volume of the reactor increases. A plot of the data from the small reactor indicates that both the first-order

and autocatalytic rate constants are reduced. The conclusion that can be drawn at this point is that radicals which are consumed on the surface by recombinations or disproportionations are involved directly in a step leading to the disappearance of pyridine, possibly in a chain mechanism.

Table 1

Surface Effects on Rate

Entrance Concentration (mole %)	Contact Time (sec)	Large[a]		Medium		Small	
		F	r	F	r	F	r
	975°C						
0.50	0.50	.253	.0242	.145	.0139	.050	.0048
1.00	0.50	.319	.0611	.363	.0695	.212	.0406
2.00	0.50	-	-	.407	.1558	.241	.0922
0.50	1.00	.228	.0109	.231	.0110	.101	.0048
1.00	1.00	.563	.0539	.322	.0308	.220	.0211
2.00	1.00	.813	.1555	.649	.1242	.333	.0637
	1000°C						
0.50	0.50	-	-	.535	.0502	.204	.0191
1.00	0.50	-	-	.686	.1287	.266	.0499
2.00	0.50	-	-	.807	.3028	.408	.1531
0.50	1.00	-	-	.634	.0297	.337	.0158
1.00	1.00	-	-	.772	.0724	.502	.0471
2.00	1.00	-	-	.831	.1559	.552	.1035

[a]These refer to the volumes of the reactors with the surface area to volume ratios of 1.99, 2.73 and 8.97 cm^{-1} respectively for the large, medium and small. F is fraction pyridine reacted and r is rate in mmoles/l sec.

From the rate equation that best fits the data (1b), it is evident that the concentration of product(s) has an accelerating influence on the rate at 950°C and above. Experiments were carried out with 2% cyanogen in the carrier gas to see if the CN radical could contribute to this acceleration. A surprisingly large effect was found, as shown in Table 2, considering the small degree of dissociation of cyanogen, e.g. K_p at 1250°C is about 10^{-17}(5).

Table 2

Effects of Cyanogen on Rate

Temperature (°C)	Entrance Concentration (mole %)	Fraction Reacted[a] Helium	$2\%(CN)_2$
900	1.00	.095	.285
925	1.00	.234	.438
975	0.50	.236	.620
975	1.00	.322	.605

[a]Contact times are all one second. The helium data are new to compare directly with that using the carrier with cyanogen.

Again indications are that a chain mechanism may be operating since it is difficult to explain the large effect on the rate of molecular cyanogen.

Discussion and Review of Data. It is worthwhile to consider the implications of the data with regard to the reaction mechanism in view of the information previously published on this reaction. First, a comparison of the rate

Table 3

Kinetic Data Comparison

Temperature °C		Fraction Pyridine Reacted[a] Ref 2	Current
	C_o[b]	3.0 mole %	2.0 mole %
900		.10	.07
950		.48	.27
975		.58-.70	.41
1000		.72-.91	.81
	C_o	0.30 mole %	0.25 mole %
970		.14-.24	
975		-	.14
1000		-	.45
1027		.55	-

[a]Nominal contact time for all data is 0.5 sec.

[b]Initial reactant concentrations.

data of Axworthy, et al (2) and that from this program at conditions as similar as possible is summarized in Table 3. Some differences in results may arise for the following reasons: (a) the previous study used a plug-flow reactor which will give a higher extent of reaction than a stirred-flow reactor at the same contact time and temperature, (b) the concentrations were higher in the previous study due to a larger total pressure which would lead to higher extents of reaction at 950°C and above, and (c) the surface area/volume was larger ($10cm^{-1}$) for the plug-flow reactor which would result in a lower extent of reaction. However, considering the differences in reactors and conditions the consistency appears quite good. More importantly, the greater than first-order dependence of rate on initial concentration reported in Ref. 2 is in agreement with the autocatalysis found in this program. Unless the rate equation and activation energies take into account this autocatalysis, extrapolations of half lives of pyridine to flame temperatures is of questionable value.

A second concern is the products of pyrolysis. Roth (3) in a very early study of the pyrolysis of pyridine found HCN and bipyridine as the major products. Hurd and Simon (4a) reported benzene, benzonitrile, acetonitrile, acrylonitrile and quinoline as the volatile products. Axworthy et al (2) reported the same products as Ref 4a, with the addition of methane and naphthalene. This study has confirmed the production of HCN, benzene, acrylonitrile, hydrogen and some methane, although not as much as reported by Ref. 2, at least a little ethylene and buten-3yne, and possibly acetylene for the volatile products. The mixture of condensed products at the reactor exit contained species which gave rise to ions characteristic of bipyridines/biphenyl, quinoline/naphthalene and acridines in order of decreasing abundance.

Notably absent is mass spectral evidence of significant amounts of acetonitrile, or propene/propyne type species. Notably absent in the results of Ref. 2 and 4 are acetylene/ethylene and bipyridines. It is because of these differences that it is believed that additional study of the products is warranted before proceeding to the oxidation studies because this is necessary to arrive at a reasonable mechanism for the pyrolysis.

The last consideration is that of the initial rupture in the pyrolytic mechanism. Hurd and Simon (4b) have suggested the primary step in the pyrolysis is the ring rupture. An estimation of the bond energies in the pyridine molecule would lead to the conclusion that ring rupture is less likely than C-H breakage. Using the atomization energies and information reported by Dewar, et al (6), and assuming the C-H and C-C bond energies in pyridine are the same as in benzene, 102.4 and 117.2 kcal/mole respectively, the C-N bond energy is calculated to be 106.5 kcal/mole. This leads to the conclusion that if only a single bond is to be broken initially, the C-H is more likely to break. This does not preclude the possibility that multiple bond ruptures to form stable molecules (e.g. HCN and CH_2CHCCH) may be less endothermic than a single bond rupture.

The activation energies for the first-order constants that have been reported, 70 kcal (Ref 2) or 48 kcal (Ref 1), are well below the bond energies involved and cannot represent simple homogeneous bond rupture. Thus, the reaction could be surface initiated, for which there is no direct evidence at this time, or a chain mechanism. The activation energy for the autocatalysis constant of 112 kcal, is in the ring bond strength region. Thus, this rate term may represent ring fragmentation. It should be noted that the 112 kcal is on apparent upper limit for the activation energy since in the treatment of the rate data the catalytic concentration was assumed proportional to the concentration of pyridine decomposed and that the proportionality constant

was temperature independent. This assumption could be in error since some products increase in relative yield as the temperature increases, e.g. if the relative yield of catalyzing product doubled from 950 to 1000°C then the E_a for this term could be reduced by 40 kcal.

In addition, the analyses of the solids from the reactor exit showed almost entirely aromatic type compounds, e.g. the mass spectral data discussed earlier and the nmr data which indicated 80 to 90% of the hydrogen signal in the aromatic region (1c). Thus, the following question can be raised: if ring rupture is the major means by which pyridine initially reacts, would the most likely products be complex aromatic species, or would additional C-C breakage occur leading to a larger fraction of volatile products? It should be noted that the total area under all of the volatile product peaks is less than that under the remaining pyridine peak after 95% reaction, which indicates that the overwhelming bulk of the products are less volatile than pyridine. The tentative conclusion reached at this time by this investigator is that initiation probably involves both C-H and C-N bond rupture followed by radical attack on reactant to produce new radicals which can go on to form product and/or other radicals to continue the chain, possibly similar to a polymerization chain with chain termination on the walls. It must be stressed that these ideas are still in the formative stages, the process is not clear at the molecular level and the low activation energy of the first-order term still presents a problem.

It is of interest to note the results of pyrolytic studies of acetylene (7), benzene (7b,8) and diacetylene (9). All three species are thought to decompose by chain mechanisms; the first two gave rate equations with first- and second-order terms, the third was second-order. For benzene the first-

order term had an activation energy of about 52 kcal, similar to that for pyridine from this study. The product analyses for those reactions were far from complete but the partial results from more than one study show that the major product from acetylene is benzene, with some diacetylene, buten-3yne, methane, ethylene, hydrogen, naphthalene, styrene, etc. From [illegible]zene, hydrogen, diphenyl, acetylene, diacetylene and tars were obtained. From diacetylene, acetylene, methane, ethylene, buten-3yne, hydrogen and carbon were obtained, notably no aromatics were reported. With this additional information, the probable origin of several of the products from the pyridine pyrolysis can be assumed.

Work is continuing on this complex mechanism.

Task 4

The rate of oxidation of cyanogen was measured at two additional concentrations, the results were consistent with those reported previously (1c). The data will be included in a later report when there has been additional accumulation.

Tasks 1, 3, 5 and 6.

Task 1 will be complete with the assembly of the quadrupole mass spectrometer, which has been postponed because of the product analyses currently being carried out; the others will be undertaken at a later date.

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